Special Conference Deals With Cadmium Alternatives

By James H. Lindsay, Contributing Technical Editor

n October of last year, a workshop-style conference, Advanced Techniques for Replacing Chromium: An Information Exchange took place in Johnstown, PA. It was conducted by the National Defense Center for Environmental Excellence (NDCEE), operated for the government by Concurrent Technologies Corporation in Johnstown. Following on the success of that meeting, on May 24-25, 1995, the NDCEE held another conference, Cadmium Alternatives: An Information Ex*change*, which addressed cadmium issues in an identical format. As with the chromium meeting, the event was co-sponsored by the American **Electroplaters and Surface Finishers** Society (AESF), the U.S. Environmental Protection Agency (U.S. EPA), the National Center for Manufacturing Sciences (NCMS) and the Society of Vacuum Coaters (SVC).

The NDCEE is connected with the United States Department of Defense. Its primary goal is to lead and support the military **and** the commercial industrial base in the transition to environmentally acceptable manufacturing technologies. The Johnstown Center provides a site for testing, evaluating and applying new environmentally safe technologies in a lowrisk setting.

In the field of surface finishing, expertise is available to demonstrate technology in the following areas:

- Metal plating waste reduction
- Chlorinated solvent cleaning alternatives
- Environmentally acceptable painting systems
- Clean corrosion and wearresistant coating systems
- Clean maintenance and refurbishment systems

Another goal of the NDCEE is to serve as a national resource for environmental technology information. Recognizing the importance of cadmium in commerce, the NDCEE organized this meeting to provide a forum for discussing ways to reduce the use of electrodeposited cadmium. Representatives from industry, the military and regulatory agencies described their ongoing projects to eliminate cadmium usage in a variety of applications. The problems encountered in finding and qualifying alternatives were also considered.

The first day of the two-day conference consisted of presentations on a variety of materials and processes, the contents of which make up the bulk of this article. Most of the second day was devoted to roundtable discussions, which were very productive.

Several of the presentations dealt with specific alternatives to cadmium. Among the most common were zinc alloys, tin alloys and ion vapordeposited (IVD) aluminum. Several others were also noted during the course of the workshop. In addition, several companies and agencies covered their overall programs for cadmium replacement or reduction.

Why Cadmium?

Cadmium has been used in commerce for many decades. Its been used primarily in corrosion-resistant coatings, pigments for paints and plastics, and as the cathode in nickelcadmium batteries. Its properties have offered many engineering advantages. First and foremost is its good corrosion resistance, and the fact that when corrosion does inevitably occur, its corrosion products are not voluminous. Besides that obvious advantage, it offers a low coefficient of friction, low electrical resistivity, good solderability and good appearance for decorative applications. It also offers

excellent resistance to hydrogen embrittlement during processing. Unfortunately it has been found that, while many materials offer some of these desirable characteristics, no one substitute material offers all of these properties.

Health Effects

To begin the workshop, Dr. Robert Elves, of Concurrent Technologies Corporation, gave an overview of the health hazards associated with cadmium exposure. The human body can be exposed to cadmium in many ways. Occupational exposures come in the form of cadmium dust and fumes. Non-occupational exposure can come naturally in foods (10-40 µg/day), and through cigarette smoking.

Short-term exposure can result in nose and throat irritation from dust and fumes, with delayed "chest cold" symptoms if inhaled. Death can result if the dose is sufficiently high (1 hr at 40–50 mg/m³; 5 hr at 9 mg/m³). Longterm exposure can lead to ulceration, emphysema, anemia, bone damage, kidney damage and lung cancer.

Current OSHA Action Levels for air quality are set at $2.5 \ \mu g/m^3$; exceeding this level initiates compliance activities. The OSHA eight-hr Time-Weighted Average Personal Exposure Limit (TWA PEL) is $5 \ \mu g/m^3$. These limits affect 525,000 general industry and construction workers, and have prevented 27 cancer deaths and 270 cases of kidney disease. The annual compliance cost is reported at \$200 million.

Industrial

& Government Programs The Department of Defense has an ongoing program on cadmium uses and replacement activities, as described by James Folck, from Wright-Patterson AFB. The importance of this program is clarified when one realizes that, at one time, every piece in an aircraft landing gear was cadmium-plated or, in some cases, chromium-plated. For structural members, short-term cadmium alternatives are IVD aluminum, dry film lubricants and metal-ceramic coatings. Further out, the substitute is zinc-nickel. For fasteners. short-term replacements involve dry film lubricants and greases. For the midterm, zinc-nickel plating with a dry film lubricant is the system of choice. Tin-nickel plating poses an alternative for the longer term.

The U.S. Army Program for cadmium elimination was discussed by Jason Wright of Ocean City Research Corporation (Alexandria, VA). With this ongoing program, the Army is:

- 1. Depleting its existing stock of cadmium-containing parts and
- 2. Specifying new systems without cadmium products.

Army depots have introduced alternative processes such as ion vapor deposition, ion implantation and zinc-nickel plating. The emphasis is on replacing cadmium without affecting military readiness.

At Johnstown, the NDCEE has an ongoing cadmium plating alternatives program. Described by David Schario of Concurrent Technologies Corporation, the program is a response to the EPA 33/50 program, which calls for industry to voluntarily reduce cadmium usage. Cadmium plating cannot be replaced with one alternative; it must be application-specific, because no substitute can provide all the "cadmium-like" properties. The NDCEE project is identifying, from documented data and validation results, the characteristics of acceptable cadmium alternatives. From this information, a database will be developed so that design engineers and specifiers can develop the best alternative for the given application. This project is not intended to develop new processes, but rather to facilitate the use of existing ones.

Zinc Alloys

Jerry Jones of Tinker AFB, Oklahoma City, OK, outlined a comprehensive coating validation program undertaken after cadmium plating was discontinued in 1991. The primary focus was on zinc alloys, including zinc-based cobalt, tin, iron and nickel and, where applicable, from alkaline and acid electrolytes. Plate and rod specimens were examined, as well as threaded fasteners. Samples were evaluated for corrosion-resistance, abrasion resistance, fatigue life, torque tension (for threads), hydrogen stress cracking and the usual coverage uniformity and thickness capabilities. The test data indicate that zinc-nickel from the alkaline bath met or exceeded results for cadmium plating in all areas of study. The other alloys also out-performed cadmium in many areas, but the alkaline zincnickel ranked first.

Another zinc-nickel talk was presented by Edward Budman of Dipsol Gumm Ventures, a supplier of zinc-alloy plating processes. He stressed the advantages to be gained by substituting zinc-nickel for cadmium, as opposed to a pure zinc coating. Salt spray and cyclic corrosion data were presented for chromated and non-chromated zincnickel alloy. The process characteristics for acid and alkaline zinc-nickel systems were compared.

Gary Loar, of McGean-Rohco, gave another supplier's viewpoint of zinc-nickel plating as a cadmium alternative. Acid and alkaline solutions were again compared, and Loar noted that different applications might require one or the other type of bath. He noted that many of the disadvantages experienced with older lownickel alkaline baths can be overcome with new high-nickel (~12 percent) baths. As a trade-off, chromating is more difficult, but newer chromates may address these concerns.

Tin Alloys

Several speakers reported on tinbased alloys, particularly tin-zinc electrodeposits. Alain Adjorlolo, of the Boeing Defense & Space Group, discussed studies of zinc-nickel and tin-zinc, with emphasis on the latter. He reported good results for corrosion, paint adhesion, electrical contact resistance and hydrogen embrittlement resistance. Current efforts are directed toward finding an optimum alloy composition to give the best threaded fastener lubricity. There is also a testing program underway that deals with the reembrittlement tendencies in specific aircraft fluids.

Dr. Don Snyder, of Atotech USA, Inc., discussed two tin alloys-tinnickel and tin-zinc. He noted that tinzinc offers an essentially pore-free, fine-grained deposit that is semibright-to-satin in appearance. The corrosion-rate data presented showed that 80/20 tin-zinc was better than cadmium, zinc or 70/30 tin-zinc alloy. Dr. Snyder noted that the alloy combined the barrier protection properties of tin with the galvanic protection of zinc. The tin-nickel (65/ 35) alloy was shown to provide good corrosion resistance in both environmental and accelerated testing. In terms of mechanical properties, wear resistance data were comparable to that for hard chromium. The deposit also exhibited a low friction coefficient and was non-magnetic.

In a second presentation, Budman also discussed tin-zinc alloys. He noted that several systems were available, based on alkaline, neutral and acidic electrolytes. Gearing his talk to the neutral pH bath, he noted advantages in solderability and corrosion resistance with those coatings. Chromates were found to work on alloys containing up to 80 percent tin. Higher percentage tin alloys were difficult, if not impossible, to chromate. Tin-zinc alloys show promise of greater acceptance as an alternate to cadmium plating.

Ion Vapor Deposited Aluminum

Ion vapor deposited aluminum has been in commercial use for more than 20 years. With the concern over cadmium, it has found use as an alternative coating. Sheldon Toepke, of McDonnell Douglas Corporation, discussed IVD aluminum as a leading candidate to replace cadmium. McDonnell Douglas pioneered the development of IVD aluminum many years ago. Toepke noted that IVD aluminum offers excellent corrosion resistance, without causing hydrogen embrittlement or reducing the mechnical properties of the substrate.

Jack Dini, of Lawrence Livermore Laboratories, gave a good discussion on ion-plated coatings. Because such

systems are being considered as alternatives to cadmium, it is good to know what can be done with such coatings in a general sense. It was stressed that a primary advantage of the ion plating process is the excellent adhesion obtained as a result of the high energies imparted to the coating metal. The surface morphology of such deposits can be altered by varying deposition parameters, such as chamber pressure and applied voltage. Such changes in morphology, Dini noted, can noticeably influence the corrosion resistance. Misapplication of such parameters can make a very poor IVD coating.

A related physical vapor deposition technique, using cathodic arc evaporation, was described by Dr. Anthony Perry, of ISM Technologies, San Diego, CA. Cathodic arc evaporation produces highly ionized vapor in a vacuum chamber. Dense, adherent coatings with low residual stress can be produced by this method.

Other Alternatives

Several other alternatives to cadmium were discussed at the meeting. Michael J. Narush, of Metal Coatings International, Shelby Township, MI, discussed some novel dip-spin or spray-coated coatings for automotive fasteners. The system involves an inorganic film of zinc, aluminum and metal oxides, sealed with a silicatebased friction-modifying topcoat. Success as a cadmium substitute on fasteners has been demonstrated in a joint program with a major U.S. automotive company. Both corrosion and torque tension test results meet the required specifications.

Mark Mosser, of Sermatech International, Limerick, PA, described some aluminum-ceramic coatings as alternatives to cadmium. They were originally intended for turbine engine applications as replacements for silicone-aluminum paints, silicone enamels and nickel-cadmium plating. They were a natural for aerospace cadmium replacement in hightemperature, saline and corrosive environments. Again, these coats are applied by spray, and cured at relatively low processing temperatures (~160 °C). Properties were said to compare favorably with cadmium. In applications requiring lubricity, however, a wax lubricant is required.

A View From The Other Side

To offer a balanced viewpoint to the cadmium issue, Hugh Morrow of the International Cadmium Association was invited to present the views from the cadmium industry. Following is the abstract of the paper that he submitted, entitled "Cadmium Coatings Have a Future."

"Twenty-five years ago, the human health and environmental concern over cadmium coatings may have been justified. About half of western world cadmium consumption was utilized in coatings; control of occupational exposures was not required below 200 µg/m³; electroplating process wastes were usually landfilled; water effluent guidelines for cadmium did not exist; and little or not [sic] attempt was made to recycle or recover cadmium from coated products. All these concerns have changed dramatically in the past 25 years.

"Today, cadmium coatings account for less than 10 percent of total western world cadmium consumption, but continue to offer the same excellent combinations of corrosion plus lubricity, low electrical resistivity, or solderability and a variety of other engineering advantages that they always have. In addition, cadmium coatings now enjoy environmental advantages which they didn't have 25 years ago. Occupational exposures in cadmium plating shops are below the new OSHA Action Level of 2.5 μ g/m³, the world's strictest cadmium standard. Water effluent guidelines are so low as to virtually preclude any water pollution, land disposal of cadmium sludges is prohibited, air emissions are non-existent, and wastes from cadmium plating operations and product disposal are now collected and recycled.

"The combination of these engineering and environmental advantages indicates that there is no basis to require substitutes for cadmium coatings in those applications where its use has been shown to be irreplaceable. It is suggested that a far more fruitful approach to protecting the environment with respect to cadmium coatings would be to encourage recycling rather than searching for substitutes."

Discussion Sessions

One of the good features of this workshop and the earlier one on hexavalent chromium was the edict that no questions were allowed during the presentations. Not only did this allow the audience to hear the author's entire line of reasoning without interruption; it also allowed the audience time to absorb what the person was trying to get across, without the sound of grinding axes. After having some time for thought, the audience could raise comments and questions during the discussion sessions. Of course, the discussion would involve those participants with the greatest interest in the topic and would be conducted with the perspective of having heard all of the presentations. Generally, this format worked out very well.

The discussion sessions included such topics as:

- · Issues for replacing cadmium
- Specification change requirements
- Corrosion testing
- Torque tension tests for threaded fasteners
- Hydrogen embrittlement during and after plating
- Zinc-nickel electroplating (acid versus alkaline)
- Non-electroplating process issues

The discussion on replacing cadmium was rather wide-ranging. The largest issue in changing specifications is economics. Surprisingly, much of the cost is tied up in paper. One participant noted that the costs of changing one manual on a system that requires several hundred manuals can add up to hundreds of thousands of dollars. (True!)

Another issue was the validity of current test methods. Several people suggested that traditional performance tests may not be as pertinent for some of the newer alternatives. Finally, there was an interesting dialogue on the problems with cadmium already plated on parts. Such parts occasionally need to be washed and some cadmium finds its way into waste streams. Furthermore, there is the question of toxic waste generated by the stripping of existing cadmium plate. The questions go on.

The discussion of specification change requirements generated

interesting comments. Specifications in older, military contract work are hard to change for a variety of reasons, including part identification and the aforementioned paperwork costs. New contracts are easier to change, particularly those involving non-critical parts. With these situations, there is much more freedom to change, as the work is systemoriented, rather than part-specific.

Corrosion test discussions stressed the inability of traditional salt spray testing to predict corrosion in the field. There is a need for an industrystandardized, cyclic test to be used in the search for cadmium alternatives. An interesting question arose on the effect of removal of chromate conversion coatings by regulatory fiat. After all, these are hexavalent chromium processes that also are environmentally wanting. Some of the most successful cadmium alternatives, including IVD aluminum, depend on chromates to provide the required corrosion resistance.

Hydrogen embrittlement is an important issue in consideration of

any cadmium alternative. The session participants heard a cardinal point made when it was noted that inservice corrosion can be a source of hydrogen, regardless of the lack of hydrogen in a workpiece's processing history. Even cleaning solutions can be an in-service source of hydrogen. The workshop participants concluded that the best methods for avoiding hydrogen embrittlement are to:

- 1. Select a substrate that fails in a ductile, rather than brittle, manner in the service of interest;
- 2. Use cadmium substitutes that will not galvanically drive excess hydrogen; and
- 3. Observe good processing practices.

On the issue of acid vs. alkaline zinc-nickel plating, a comparison of the two processes showed advantages for either one, depending on the nature of the application. Function is the primary concern—the acid bath is best for continuous strip, high speed and simple shapes, while the alkaline process is the best for irregularly shaped, racked or barrel-plated articles, because of throwing power advantages and other things.

In all, *Cadmium Alternatives: An Information Exchange* was a rewarding forum for those who participated. It was an excellent follow-up to the successful forum on hexavalent chromium alternatives conducted last year. These are important issues in current times, and such events provide an opportunity to learn and exchange ideas in an ideal format and setting.

About the Author



Dr. James H. Lindsay is a research engineer with General Motors Research Laboratories, 30500 Mound Rd., Warren, MI 48090-9055. He is a

contributing technical editor for P&SF; immediate past vice chairman, publicity, AESF Research Board; and member of the Scientific Achievement Committee.